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NOx Formation in CO Flames

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16. ABSTRACT The report gives results of an experimental study to determine if early NO and NO2 can be observed in CO flames, since prompt NO is not anticipated and since HO2 levels might be expected to be lower in CO flames. (Previous studies of NO and NO2 production in methane flames with and without fuel nitrogen suggested that the early appearance of NO2 results from the fast reaction of NO + HO2 = NO2 + OH.) CO flames containing NO, ammonia, and cyanogen were profiled for NO and NO2 in this study. Effects of flame temperature and of nitrogen- and argon-"air" were also examined. The results give evidence for prompt NO in CO flames as well as for early NO2. The prompt NO and early NO2 levels are less than in methane flames, but the same mechanism appears to explain the formation of NO2 in both flame systems. In most instances, the quantity of NO or fuel-nitrogen added to the flames can be accounted for as NO, NO2, and an unidentified nitrogen species. Analysis of the rates of depletion of ammonia and cyanogen in the CO flames yields Arrhenius coefficients equivalent to 58 and 41 kcal/mole, respectively.

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NO_x FORMATION IN CO FLAMES

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ABSTRACT

An experimental study was undertaken to determine whether early NO and NO_2 could be observed in CO flames. Earlier studies have suggested that prompt NO is not anticipated in CO flames; also HO_2 levels might be expected to be lower in CO flames. Previous studies of the production of NO and NO_2 in methane flames, with and without fuel nitrogen, suggest that the early appearance of NO_2 comes from the fast reaction of $NO + HO_2 = NO_2 + OH$. CO flames containing NO, ammonia, and cyanogen were profiled for NO and NO_2 in this study. Effects of flame temperature and of nitrogen- and argon-"air" were also examined. The results give evidence for prompt NO in CO flames as well as for early NO_2. The prompt NO and early NO_2 levels are less than in methane flames, but the same mechanism appears to explain the formation of NO_2 in both flame systems. In most instances the quantity of NO or fuel-nitrogen added to the flames can be accounted for as NO, NO_2, and an unidentified nitrogen species. Analysis of the rates of depletion of ammonia and cyanogen in the CO flames yield Arrhenius coefficients equivalent to 58 and 41 kcal/mole, respectively.

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SECTION I

INTRODUCTION

It is well recognized today that there are two sources of nitrogen oxides (NO_x), namely that produced by thermal fixation processes via the Zeldovich mechanism, and that produced by oxidation of organic nitrogen compounds in fuel (fuel-bound nitrogen). Recent studies by the authors and by other investigators have shown that fuel-bound nitrogen yields high and varying amounts of NO in combustion product gases (1-7)*. More recently, the authors have shown that NO and NO_2 are produced in flames by a mechanism that differs from both the Zeldovich and the general fuel-bound nitrogen mechanisms, and that this new mechanism may be important in the development of other NO_x mechanisms (8). One of the objectives of the present study has been to determine how well and to what extent this new mechanism lends itself to CO flames.

The Zeldovich mechanism as used to explain the formation of NO in post-flame combustion processes is as follows:

$$O + N_2 = NO + N \quad (1)$$

$$N + O_2 = NO + O \quad (2)$$

$$O + O + M = O_2 + M \quad (3)$$

$$N + OH = NO + H. \quad (4)$$

More recently, however, Fenimore (9) has indicated that NO can be formed early and rapidly in hydrocarbon flame systems to produce what he has termed "prompt" NO. In hydrocarbon flames, he suggests that the early NO can arise from oxidation of species such as CN and HCN produced in the flames. It follows from these same arguments that fuel-nitrogen compounds

* References are listed on page 28.

will yield NH and CN species, i.e., N, NH, NH_2, CN, HCN, etc., which will be oxidized to NO in flames.

In the recent flame studies at Battelle-Columbus it has been observed that NO and NO_2 are produced early in methane-air flames, with and without fuel-bound nitrogen additives, and that this NO_x may be different from Fenimore's "prompt" NO. In some instances, NO_2 has been observed in the visible flame region prior to the appearance of NO. A mechanism has been developed which suggests that NO produced in the flame process is scavenged by HO_2 radicals, producing "early NO_2". This early NO_2 is then converted to NO via reactions with excess O-atoms in the flame. The mechanism used to explain this phenomenom is as follows,

$$NH,\ CN + O_2 = NO + OH,\ CO \qquad (5)$$

$$NO + HO_2 = NO_2 + OH \qquad (6)$$

$$NO_2 + O = NO + O_2. \qquad (7)$$

In order for HO_2 to scavenge NO in the visible flame this mechanism requires that Reaction 6 have a fairly high rate constant and the concentrations of HO_2 be of the order of 10-50 ppm in the flame. Analysis of conditions in methane flames has indicated that the oxidation of formaldehyde and CHO radicals could yield the necessary level of HO_2 radicals. A principal question in the current study concerned whether or not the level of HO_2 radicals would be high enough to convert NO to NO_2 in CO flames.

CO FLAME KINETICS

The oxidation mechanism of CO in flames is well established to proceed as follows,

$$CO + OH = CO_2 + H \qquad (8)$$

$$O + H_2 = OH + H \qquad (9)$$

$$H + O_2 = OH + O \qquad (10)$$

$$O + H_2O = OH + OH \qquad (11)$$

$$H + H_2O = H_2 + OH. \qquad (12)$$

One cannot present a CO oxidation mechanism without including oxidation reactions for hydrogen since it is well known that the direct oxidation of CO by oxygen

$$CO + O_2 = CO_2 + O \qquad (13)$$

is slow, if it goes at all (10).

In accord with the interests of this study is the role of the hydroperoxyl radical. The HO_2 has often been excluded from oxidation mechanisms, as noted above, on the basis of its being of minor significance at flame temperatures. More recent studies, however, indicate that the HO_2 radical can play a significant role in hydrocarbon oxidation (11). The current issue is, how important is the HO_2 radical in NO_2 production from CO flames?

In hydrocarbon flames, HO_2 will result from the extraction of hydrogen from methane, from aldehydes and from other intermediates produced in the oxidation processes,

$$CH_4 + O_2 = CH_3 + HO_2 \qquad (14)$$

$$CH_2O + O_2 = CHO + HO_2 \qquad (15)$$

$$CHO + O_2 = CO + HO_2. \qquad (16)$$

On the basis that formaldehyde and subsequent CHO radical levels are less in CO or CO-H_2 flames, it may well be that early NO_2 and prompt NO would also be significantly less in CO or CO-H_2 flames. (Fenimore reports no prompt NO in CO or H_2 flames.)(9)

In the present study, the CO flames were stabilized by adding water vapor to the cool preflame gases. In water-stabilized CO flames any HO_2 radicals must form either directly or indirectly from the added water vapor. One might consider the production of HO_2 radicals by extraction of hydrogen from the water molecules,

$$H_2O + O_2 = HO_2 + OH. \qquad (17)$$

This reaction, however, requires about 72.7 kcal of enthalpy at 1000 K. Equilibrium calculations show that, at most, only a few ppb HO_2 would exist

at this temperature. A more likely reaction producing HO_2 is obtained indirectly from the hydrogen atoms derived from Reaction 8. Thus, the three-body reaction

$$H + O_2 + M = HO_2 + M, \qquad (18)$$

could occur in the 1 atmosphere CO flames leading to several ppm of HO_2. For example, a flame containing only 3 percent O_2 and a few ppm H at 1400 K could at equilibrium have as much as 35 ppm HO_2 present.

SECTION II

EXPERIMENTAL PROCEDURES

Flat, disc-shaped laminar flow CO flames were probed using the micro-probing technique described in previous studies (12). The flames were stabilized at 1 atmosphere pressure on 1-inch and 2-1/2-inch-diameter stainless steel burners, the smaller burner providing higher flame temperatures than the larger one. Fuel-rich, stoichiometric and O_2-rich flames were probed using nitrogen or argon as a diluent. Cyanogen (C_2N_2), ammonia (NH_3), and nitric oxide (NO) were added at concentrations of 15-350 ppm to the cold gas ($CO-O_2-N_2/Ar$) mixtures.

A small 1/4-inch-I.D. water-cooled quartz probe with a 100-micron orifice in the tip was used to withdraw samples from below, in and above the flames. The pressure in the probe was 2-4 torr. The sample line from the probe was split to provide simultaneous sampling for a chemiluminescence instrument and a mass spectrometer. NO, NO_2, and the fuel-N additives were analyzed in the chemiluminescence instrument, using stainless steel and carbon converters. A quadrupole mass spectrometer was used to analyze for CO, CO_2, O_2, N_2, Ar, and H_2O. The C_2N_2 depletion was also followed on the mass spectrometer. The conversion of C_2N_2 and to a lesser extent the ammonia to NO in the stainless steel converter was not as complete as desired. Thus, these data are less reliable. Some of these fuel-N profiles were also generated by the mass spectrometer.

Flame temperatures were recorded for each flame composition used. Silca-coated Pt - PT + 10 percent Rh thermocouples (2-5 mils dia.) were used in the temperature probings.

SECTION III

RESULTS

The results presented here are drawn primarily from the profiles of NO, NO_2, and fuel-N for the various flame systems. A complete set of these profiles for all flames probed is presented in Appendix A.

Table 1 lists the pertinent data for the 24 flames probed in this study. In the numbering system used, the odd number flames were O_2-rich flames and the even number flames were fuel-rich or near stoichiometric flames. The NO and NO_2 data are given in terms of ppm conversion of fuel-N to NO and NO_2.

The smaller 1-inch-diameter flames are the hotter flames and are referred to as the Hi-temp flames; the 2-1/2-inch-diameter flames are the lower temperature flames and are referred to as the Lo-temp flames. Temperature differences between the two flames ranged from 215-260 C. Cold gas velocities ranged from 13.3-17.2 cm/sec in the Hi-temp flames and from 5.8-7.9 cm/sec in the Lo-temp flames.

Complete oxidation of CO to CO_2 occurred only in the oxygen-rich flames. Some CO remained unoxidized in the postflame gases of the stoichiometric and fuel-rich flames. Consequently, these latter flames had lower maximum flame temperatures than did the corresponding O_2-rich flames.

CO FLAMES - NO ADDITIVES

Initially, additive-free CO flames containing argon as a diluent were probed to determine the extent of N-containing impurities in the original composition gases. No NO or NO_2 was observed in these flames, indicating

TABLE 1. NITROGEN OXIDE DATA FROM CO FLAMES

Flame No.	Flame Composition (mole fraction)					Max Temp, K	Additive		Maximum Observed Conversion of Fuel-N to		NO_2 Consumed in Postflame, percent
	CO	O_2	H_2O	N_2	Ar		Species	ppm	NO (ppm)	NO_2 (ppm)	
1-Inch-Diameter Burner (High-Temperature Flames)											
1	.190	.155	.017	.638	—	1609	None	—	12.5	0	0
2	.202	.104	.018	.676	—	1516	None	—	32	4	100
3	.187	.154	.017	.642	—	1609	NO	35	50	17	100
4	.199	.102	.018	.681	—	1516	NO	36	61	16	100
5	.187	.153	.017	.643	—	1609	NH_3	43	53	3.0	100
6	.153	.099	.033	.675	—	<1516	NH_3	32	37	1.6	100
7	.183	.156	.039	.622	—	<1609	C_2N_2	125	260	4.0	100
8	.193	.099	.033	.675	—	<1516	C_2N_2	165	295	2.5	100
9	.160	.131	.015	—	.694	1593	NO	92	113	14	100
10	.168	.087	.011	—	.734	1509	NO	71	61	15	100
11	.162	.133	.015	—	.690	1593	NH_3	65	56	28	75
12	.162	.083	.014	—	.741	1509	NH_3	62	86	14	72
13	.160	.131	.015	—	.694	1593	C_2N_2	300	565	9	100
14	.168	.087	.011	—	.734	1517	C_2N_2	350	690	5	100
2-1/2-Inch-Diameter Burner (Low-Temperature Flames)											
15	.217	.135	.014	.634	—	1582	None	—	4.3	4.3	65
16	.238	.085	.010	.667	—	1422	None	—	5.6	3.8	27
17	.158	.117	.014	.711	—	1370	NO	48	34	34	86
18	.168	.073	.010	.749	—	1296	NO	34	25	18	100
19	.113	.082	.020	—	.785	1348	NO	36	31	28	88
20	.117	.051	.014	—	.818	1271	NO	64	49	23	100
21	.113	.082	.020	—	.785	1348	NH_3	35	35	30	83
22	.117	.051	.014	—	.818	[illegible]	NH_3	36	39	12	100
23	.113	.082	.017	—	.788	[illegible]	C_2N_2	122	125	13	81
24	.117	.051	.014	—	.818	1271	C_2N_2	129	120	9	100

essentially nitrogen-free cold gas mixtures. Substituting N_2 for argon in the additive-free flames resulted in significant nitrogen oxide formation. These flames, Flames 1, 2, 15, and 16, provide baseline data for the Hi- and Lo-temp CO flames probed in this study. As seen in the data, all of the flames with N_2 as a diluent produced NO and all but one of these flames produced small but measurable quantities of NO_2. The low-temperature flames, Flames 15 and 16, although at a higher temperature than Shaw and Thomas' additive-free CO flames (13)(which were <1100 K) yielded about the same NO_x levels:

Shaw and Thomas	6-12 ppm
This work	9-10 ppm.

Reducing the oxygen content of the Hi-temp flame to near stoichiometric conditions produced about 4 ppm NO_2 early in the flame reactions, but the NO_2 was subsequently consumed in the postflame region leaving only NO in the emission gases as shown in the Flame 2 data. Thus, in both O_2-rich and near stoichiometric Hi-temp CO flames without additives only NO is present in the postflame gases. The stoichiometric flame produced more than twice as much NO as did the oxygen-rich flame.

In the additive-free Lo-temp flames, 15 and 16, the formation of both NO and NO_2 was observed in small but comparable quantities. The NO_2 was formed early in the preflame region and peaked in the early postflame zone. (In these discussions "flame" refers to "visible flame".) Consumption of NO_2 began in the postflame gases but did not go to completion in either the O_2-rich or fuel-rich flames. Appreciable amounts of NO are formed only after the NO_2 has peaked, as was also observed in the stoichiometric Hi-temp flame. Also similar to the Hi-temp flames is the production of larger quantities of NO in the Lo-temp flames under reduced oxygen conditions. In contrast to the Hi-temp flames, however, both NO and NO_2 are present in the postflame gases of the Lo-temp flames, although concentrations are low. As one might expect, the rates of formation and depletion of NO and NO_2 are somewhat slower in the cooler flames than in the hotter flames.

Post flame NO - Zeldovich Mechanism

The NO data for additive-free CO and CH_4 flames are plotted in Figure 1 as a function of time. Data from the CH_4 flame are included here only for comparison. The postflame NO values have been extrapolated to zero time which, as discussed later, may give some indication of the contribution of non-Zeldovich processes to NO formation in the flames. Extrapolation of the postflame NO data in both the CO and CH_4 flames produced positive intercepts. It is quite obvious, however, that the intercept value is much higher in the CH_4 flames, as is also the initial rate of NO formation. The positive intercepts here suggest the presence of prompt NO in both flame systems. The presence of prompt NO in CO flames is contrary tc Fenimore's original observations.

CO FLAMES WITH ADDITIVES

The three additives, NO, NH_3, or C_2N_2, were selected for their different bonding characteristics of the N-atoms. Each additive has been examined in terms of its effect on nitrogen oxide chemistry in flames.

NO Addition

Previous studies of hydrocarbon flames using NO as an additive indicated the presence of a species in the region of the visible flame which readily oxidized NO to NO_2. Nearly quantitative conversion of NO_2 was observed. NO was added to the preflame gases of $CO-O_2$ flames to determine if these same conditions also exist in CO flames. The data are presented in Flames 3, 4, 9, 10, and 17 through 20 in the appendix. The NO added to these flames ranged from about 34 to 92 ppm.

The profiles for these flames indicate that the NO added to the CO flames is depleted to various degrees as it approaches the hot visible flame region; the extent of depletion depends on the flame condition, and is generally greater in the Lo-temp flames than in the Hi-temp flames. The rate of consumption of NO is slower in the Lo-temp flames as seen in comparing the data (Flames 3, 4, 9, 10 with Flames 17 through 20). This, and the greater extent of depletion in the Lo-temp flames is likely due to

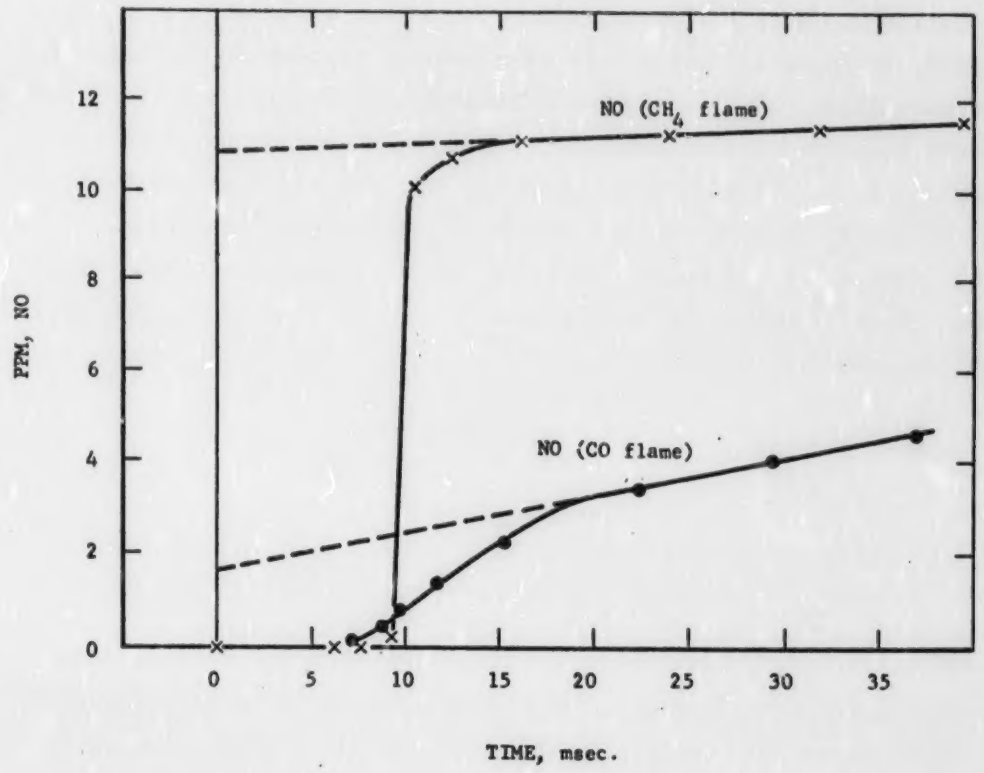

Figure 1. Extrapolation of postflame NO data to zero time

the lower temperatures and longer residence times encountered in these flames.

The important observations in the flames with added NO are that in all cases the NO is consumed as it approaches the hot visible flame and that this consumption is followed by a corresponding formation of NO_2. The NO_2 thus formed reaches a peak value coincident with the minimum in the NO curve. The NO_2 is then consumed to varying degrees in the postflame region with subsequent reformation of the NO. All of this points to direct formation of NO_2 from the added NO. Thus a strong oxidant, presumably HO_2, exists in the CO flames.

The above trends in NO and NO_2 in the CO flames with added NO are similar to those observed in hydrocarbon flames with added NO, although the extent of formation and depletion in each flame varies. Generally, the hydrocarbon flames convert a larger fraction of the NO to NO_2 than do the CO flames. This is likely related to the relative amount of oxidant (HO_2) present in each flame system.

NH_3 Addition

Flames 5, 6, 11, 12, 21, and 22 show the NO and NO_2 data from CO flames with NH_3 as an additive. The flames contained from 32 to 65 ppm NH_3. All flames containing NH_3 produce NO and varying levels of NO_2. Only the Lo-temp flames, e.g., Flame 21, show strong or moderate coupling (or interdependence) between the NO and NO_2 formation and depletion processes.

Variations in NO_2 levels appear related to a diluent effect as seen in the data of Flames 5 and 21. NO_2 formation is significantly less in flames containing N_2 as a diluent as compared to those with Ar as a diluent. About 10 times more NO_2 is produced in the cooler Lo-temp flame with Ar than in the Hi-temp flame with N_2 even though each flame had comparable NH_3 levels. Some NO_2 remains in the postflame gases of the Lo-temp flame, but none is left in the hotter flame.

Even though NO_2 levels vary, similar trends are observed in all flames with NH_3 - the NO_2 forms early in each flame with subsequent peaking and consumption of the NO_2 in the near postflame zone. In this respect, the early NO_2 formation pattern is the same in CO flames containing either NH_3 or NO as an additive; extent of NO and NO_2 coupling, however, can be quite different. Also, in the flames containing NH_3, the major and often only nitrogen oxide species in the emission gases is NO; the data indicate almost 100 percent conversion of NH_3 to NO in the flames. Only flames with Ar as diluent contained measurable quantities of NO_2 in flue gas. In these instances, the NO_2 concentration amounts to about 12 percent or less of the total NO_x, which is representative of many reported NO_2 levels in flue gases.

$\underline{C_2N_2}$ Addition

Flames 7, 8, 13, 14, 23, and 24 show that the NO and NO_2 data from CO flames with C_2N_2 as an additive. The level of C_2N_2 in the flames ranged from 122 to 350 ppm.

As with NH_3, all CO flames containing C_2N_2 as an additive, produce both NO and NO_2 in the early flame reactions. However, data from the flames containing C_2N_2 do not show any direct relationships (coupling) between NO and NO_2 formation and depletion. The lack of apparent coupling between NO and NO_2 formation and depletion is likely due in part to the relatively small fraction of NO_2 derived from the C_2N_2 in these flames. This is especially true in all of Hi-temp flames where only 0.7 to 1.6 percent of the C_2N_2 was converted to NO_2 in the early flame reactions. More NO_2 forms in the Lo-temp flames with Ar as a diluent as was also noted with flames with NH_3. Except for Flame 23, the NO_2 is completely consumed in the postflame region of the CO flames with added C_2N_2 leaving only NO in the flue gas.

Large quantities of NO are formed from the C_2N_2 in each flame as seen in the figures. The data indicate that the hotter flames convert nearly 100 percent of the C_2N_2 to NO, while the cooler flames less conversion to NO occurs, but at least 45 percent of the C_2N_2 appears as NO in every case.

SUMMARY OF RESULTS - FLAMES WITH ADDITIVES

NO_2 in CO Flames

All three additives, NO, NH_3, and C_2N_2, have yielded NO_2 in the CO flames. The flame diluent, argon or nitrogen, may have had some effect, however, on the amount of NO_2 observed in these flames. Thus, it was observed that negligible levels of NO_2 were produced on adding NH_3 or C_2N_2 to nitrogen-diluted CO flames.

NO, as an additive, produced consistently high NO_2 levels in the presence of N_2, ranging from 44 to 70 percent of the NO added; conversion in flames with argon as a diluent varied from 15 to 77 percent, the low of 15 percent occurring in the hotter CO-O_2-Ar flame (Flame 9). On the basis of NO_2 formation in the flames, the overall tendency for the fuel-N compounds to produce NO_2 is NO > NH_3 > C_2N_2. With the exception of Flames 9 and 10, all flames show less NO_2 formation from the fuel-N compounds, under near stoichiometric or oxygen-deficient conditions than when excess O_2 is present.

The extensive consumption of NO_2 in the postflame gases may be indirectly showing that high levels of O atoms were present in these CO flames, if, as shown in previous studies, NO_2 produced in the flame is removed by the O atoms in the postflame. It is interesting to note that in all of the Hi-temp CO flames containing fuel-N additives, except for the CO-O_2-Ar flames with NH_3, the NO_2 is completely consumed in the near postflame region leaving only NO in the exhaust gases. Even when NO_2 is present in the postflame gases (Flames 11 and 12), the fraction of NO_2 in the NO_x is small, about 11 percent in C_2-rich flame and about 4-1/2 percent in the stoichiometric flame.

Also, data from the lower temperature flames with additives show that in all of the stoichiometric or fuel-rich flames, the NO_2 is completely consumed in the postflame region; in the O_2-rich flames, from 2 to 12 percent of the total NO_x may be present as NO_2 in the postflame gases.

Thus, all CO flames with fuel-N additives produced NO_2. With the exception of the flames with NH_3, all of the NO_2 produced is subsequently consumed in the postflame region of all Hi-temp flames and in all fuel-rich Lo-temp flames, leaving only NO in the downstream gases. In the remaining flames, NO_2 levels ranging from 2 to 12 percent of the total NO_x was observed in the flue gases. Overall, the CO flames with fuel-N additives emit little or no NO_2 with respect to total NO_x. Only one flame with N_2 as a diluent, Flame 17, showed NO_2 in the flue gas. NO is the major product formed from the fuel-N compounds and may be present at concentrations ranging from about 50 to 100 percent of the fuel-N additive concentration. Higher temperatures appear to favor more complete conversion.

NO in CO Flames - Material Balance

It is apparent from the NO data in Column 10, that, in the ppm fuel-N range covered in this study (<400 ppm max), high conversion of the fuel-nitrogen to NO occurs in each case whether it be NH_3 or C_2N_2 used as the additive. The Lo-temp flames generally produced less NO than the Hi-temp flames, although the most noted differences occurred mainly with C_2N_2.

It is equally apparent from some of the flame data that nitrogen-containing species other than NO and NO_2 are also being formed in the conversion process since a material balance between fuel-N input and NO_x output is frequently not achieved, especially in the lower temperature flames where residence times are considerably longer than in the hotter flames. More experimental work is needed in this area to more fully explain the details of the paths taken in the conversion of fuel-N to nitrogen oxides.

SECTION IV

DISCUSSION

PROMPT NO IN ADDITIVE-FREE CO FLAMES

Fenimore (9) has indicated from studies of nitrogen oxide formation in flames that "prompt NO" is observed in hydrocarbon flames but not in CO or H_2 flames. Pershing, et al (14) have reported similar results from their studies. In these studies, prompt NO is defined by extrapolating NO-concentration profiles measured in the postflame zone to zero time. As noted in Figure 1, the present study suggests that prompt NO, although quite low, may also exist in CO flames.

Two explanations are offered for these observations, namely, a Zeldovich O-atom process or a Fenimore CN process. Support for a Zeldovich process to produce prompt NO lies in the high O-atom levels in CO flames (15) and the diffusivity of O atoms into the flame. The small positive intercept in Figure 1 may be explained in terms of the excess O atoms.

A second possible explanation for prompt NO in these CO flames lies in the fact that the flames in these studies were moist flames. CH radicals might readily be generated under moist conditions, which then provide a path for the production and oxidation of HCN. A typical set of reaction steps are

$$CO + H_2O = HCO + OH \quad (19)$$

$$HCO + H_2O = H_2CO + OH \quad (20)$$

$$H_2CO + O = CH_2 + O_2 \quad (21)$$

$$CH_2 + O,H = CH + OH,H_2 \quad (22)$$

$$CH + N_2 = CN + NH \quad (23)$$

$$CN,NH + O_2 = NO + CO,OH. \quad (24)$$

A more remote path may also be traced to excited nitrogen in flames (18) via

$$CO + N_2^* \rightarrow CN + NO. \quad (25)$$

Young and Morrow (16) report that CN is formed from CO in active nitrogen by reaction with an excited state of N_2 as indicated by Reaction 25.

The much higher intercept value in the CH_4 flame, however, suggests that much of the NO here is derived from non-Zeldovich processes. At the observed flame temperatures (less than 1550 K) and high initial rate of NO formation, an unrealistically large increase in O-atom concentration would be required to produce the NO by the Zeldovich mechanism. Non-Zeldovich processes are, therefore, postulated to account for the early and rapid NO formation in the hydrocarbon flames.

Although the Zeldovich process can be considered an important source of NO in CO flames without additives, data from similar flames with fuel-N additives suggest that the same type of Non-Zeldovich processes, similar to those in hydrocarbon flames, also operate and even dominate in the CO flames to produce nitrogen oxides. The mechanism involved in these processes and some equilibrium and kinetic considerations are discussed below.

FUEL-N MECHANISM

The reaction mechanism

$$CN + O_2 = NO + CO \quad (26)$$

$$CN + O_2 = NCO + O \quad (27)$$

$$NCO + O = NO + CO \quad (28)$$

$$NH + O_2 = NO + OH \quad (29)$$

$$NO + HO_2 = NO_2 + OH \quad (6)$$

and

$$NO_2 + O,H = NO + O_2,OH \qquad (30)$$

has been postulated to account for most of the NO and NO_2 formation in the CO flames with additives. These reactions can be used to explain the early formation of NO in the CO flames, as well as the formation and depletion of NO_2. Certain reactions will predominate depending on the flame conditions.

NO Addition

Data from the flames with NO additions have indicated the presence of an oxidizing species in the region of the visible flame which readily oxidized NO to NO_2. As mentioned earlier, the oxidizing species has been postulated as the HO_2 radical. The oxidation step is shown in Reaction 6. This is a reasonable selection since the reaction of HO_2 with NO is fast and has a low activation energy (17); the rate constant is given as

$$k = 2.0 \pm 0.5 \times 10^{13} \exp \frac{-1430 \pm 180}{T} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

The HO_2 radical must be formed in the CO flames either directly or indirectly from the hydrogen in the water vapor used to stabilize the flames. As brought out in the Results section, the extraction of hydrogen from a water molecule is not a likely process for producing HO_2. However, the reaction sequence

$$CO + OH = CO_2 + H \qquad (8)$$

$$H + O_2 \overset{+M}{=} HO_2 + M, \qquad (18)$$

is a likely source of HO_2 radicals. From the NO_2 levels observed, it appears that at least 25 to 35 ppm HO_2 may exist in these flames with added H_2O.

C_2N_2 Addition

Spectroscopic studies have confirmed the production of significant quantities of CN radicals from cyanogen molecules added to CO flames (18). The addition of C_2N_2 to the CO flames should, therefore, greatly increase the CN radical concentrations, thereby enhancing the effects of the CN species on nitrogen oxide formation in the flames. As seen in earlier data,

the major oxide of nitrogen formed from the C_2N_2 is NO with only 0.7 to 5.5 percent of the C_2N_2 appearing as NO_2. The NO forms early and rapidly in the flame and coincides approximately with the C_2N_2 depletion. From the relatively low temperatures encountered in the region of NO formation, it appears that reactions of low activation energy are involved in the early production of NO. Reactions 26, 27, and 28 would appear to satisfy the low activation energy requirement and are postulated to account for the early NO formation in the flames with cyanogen.

A sequence of reactions such as

$$C_2N_2 + O_2 \rightarrow 2NCO \qquad (31)$$

$$NCO + O \rightarrow NO + CO, \qquad (28)$$

involving the original C_2N_2 molecules might also be considered. Reaction 31, however, involves stable molecular reactants and would likely be too slow to contribute significantly to the NO formation especially at low flame temperatures. A more likely reaction involving cyanogen molecules is

$$C_2N_2 + O = NCO + CN. \qquad (32)$$

This reaction has been postulated as an initial step in the breakdown of cyanogen molecules in flames (19). Both NCO and CN radicals are produced in Reaction 32, and would appear to be an excellent source of radicals for Reactions 26, 27, and 28.

Basco (20), in his cyanogen studies, has suggested that 85 percent of the CN radicals react to form NCO in accordance with Reaction 21, while only about 15 percent react to form NO in accordance with Reaction 20. The NCO produced in Reaction 27 is subsequently oxidized to NO via Reaction 28. Haynes, et al (3) have suggested the reaction

$$CN + CO_2 = NCO + CO, \qquad (33)$$

might also be an additional source of NCO leading to NO production in nonhydrocarbon flames. Certainly the NCO as well as the CN radical appears to play an important role in the formation of NO in flames containing the N-C type fuel-N materials.

The very high levels of NO observed in the flames and the fact that very little NO_2 is formed in the flames containing C_2N_2 indicate that the oxidizing step as represented by Reaction 6 is of minor importance in these CO flames. The presence of HO_2 radicals or other oxidizing species in the CO flames has been confirmed in the NO addition studies. Apparently, the oxidant level is suppressed or reduced in the presence of cyanogen. The reactive CN and NCO species derived from the cyanogen molecules may be effective in reducing the concentration of the oxidizing species, as for example, in the case of HO_2

$$CN + HO_2 = NCO + OH \quad (34)$$

$$NCO + HO_2 = NO + CO + OH. \quad (35)$$

These reactions also lead to NO production which is the dominant nitrogen oxide in the flames containing cyanogen.

$\underline{NH_3}$ Additive

Adding NH_3 to the CO flames enhance the NH level in the flames (21) thereby promoting high NO levels via Reaction 29. NO_2 formation occurs in all the CO flames with added NH_3, probably through Reaction 6. However, as mentioned previously, the NO_2 formation is much greater in flames containing argon as compared to those with N_2 as a diluent. One could consider the effects of N_2 on the reaction

$$NH_2 + NO = N_2 + H_2O, \quad (36)$$

and the alternate reaction

$$NH_2 + HO_2 = NH + 2OH \quad (37)$$

with the reasoning that the N_2 diluent shifts Reaction 36 to the left thereby allowing more destruction of HO_2 radicals through Reaction 37 or a similar reaction. The reduced HO_2 level would subsequently produce less NO_2 via Reaction 6.

The importance of Reactions 36 and 37, however, is uncertain at this time. One could reason that similar flames with argon as a diluent would reverse the above trends. While there is some indication of this in the

data (Flames 5, 6, 11, and 12), full compliance with the predicted trends is not achieved.

An alternative to the above considerations which might explain the effects of N_2 and Ar on NO_2 formation in CO flames with added NH_3 is in the efficiency of N_2 and Ar as third bodies in the reactions

$$H + O_2 + M = HO_2 + M \qquad (18)$$

and

$$H + H + M = H_2 + M. \qquad (38)$$

It is apparent, to achieve the observed results, that Ar would have to be a more effective third body than N_2 in producing HO_2 radicals. Also, Ar should be less effective in the recombination Reaction 38. Reported rate constants for Reaction 18 using Ar or N_2 as a third body (22) indicate little difference in their effectiveness as third bodies. This is also borne out in general in the data from the CO flames. For example, in the CO flames containing added NO (e.g., Flames 17 and 19), one cannot distinguish any real differences in the amount of NO_2 formed using either N_2 or Ar as third bodies. Water vapor is a more effective third body than either N_2 or Ar in the formation of HO_2 via Reaction 18 (22). Overall, however, the data do not indicate water vapor as the controlling factor.

In regard to Reaction 38, reported values (21) indicate a slightly higher rate of recombination of H-atoms in the presence of N_2 than Ar. This might account for some of the observed difference in NO_2 formation in the CO flames with N_2 or Ar as diluents, but again, would not appear to be the controlling factor. Certainly the situation is more complex in the flames with added NH_3 or C_2N_2. The reason for the reduced NO_2 formation in the flames containing NH_3 and with N_2 as a diluent is not clear at this time. Additional flame probings would prove useful here.

POSTFLAME EQUILIBRIUM CONSIDERATIONS

If one considers the following equilibria involving NO and NO_2 in the postflame gases

$$NO + 1/2\ O_2 = NO_2 \tag{39}$$

and

$$NO_2 + O = NO + O_2, \tag{40}$$

calculations show that at the lower flame temperatures encountered in these studies, i.e., about 1250 K, the NO_2/NO ratio for Reaction 39, at an O_2 mole fraction of 0.04, is less than 0.01. The ratio would be much less at higher temperatures or if Reaction 40 is included. Therefore, at equilibrium at least 99 percent of the NO_x is NO. The postflame data from the Hi-temp flames and all fuel-rich Lo-temp flames also show 99 percent or more of the NO_x as NO suggesting equilibrium conditions may prevail as represented by equations 39 and/or 40. The appearance of several ppm NO_2 in the O_2-rich Lo-temp postflame gases is unexpected from the above equilibrium (and temperature-time) considerations and indicate other conditions, involving NO and NO_2 formation and depletion processes, may prevail here.

The NO in the postflame gases may, under certain conditions of temperature and O_2-N_2 levels, be equilibrated with regard to the reaction

$$1/2\ N_2 + 1/2\ O_2 = NO. \tag{41}$$

Calculations from the flames containing N_2 (0.72 mole fraction) and excess O_2 (.04 mole fraction) indicate that about 90 ppm NO could be formed at 1200 K and about 850 ppm NO at 1600 K. These calculated levels are generally higher than those observed for NO in the postflame probings and indicate that nonequilibrium conditions, in regard to Reaction 41, generally prevail here. In the fuel-rich flames, the NO could exceed the equilibrium level which would then shift Reaction 41 to the left. Overall, however, the data do not show any large decreases in NO in the postflame gases even at the high NO levels observed in the flames with C_2N_2. Therefore, the above equilibrium is apparently not dominating in the flames, or residence times and temperatures are not sufficient to establish the equilibrium conditions.

KINETICS OF C_2N_2 AND NH_3 DEPLETION

The rates of C_2N_2 depletion and the subsequent formation of NO and NO_2 in the CO flames have been examined and some apparent activation energies for the overall depletion processes involving these N-bearing species have been determined. For C_2N_2, the general overall reaction is assumed to be

$$C_2N_2 + a\ O_2 \rightarrow NO + \text{products}. \tag{42}$$

For NH_3 the reaction is taken as

$$NH_3 + b\ O_2 \rightarrow NO + \text{products}. \tag{43}$$

The reaction $NO + HO_2 = NO_2 + OH$ is also considered in the early flame reactions and is assumed to account for the early NO_2 formation. The overall rate expressions for C_2N_2 and NH_3 depletion is expressed as

$$R_{-C_2N_2} = 1/2(R_{NO} + R_{NO_2}), \text{ for } C_2N_2 \text{ depletion}, \tag{I}$$

and

$$R_{-NH_3} = R_{NO} + R_{NO_2}, \text{ for } NH_3 \text{ depletion}. \tag{II}$$

For Reaction 42 the rate equation becomes

$$R_{-C_2N_2} = 1/2\ (R_{NO} + R_{NO_2}) = k_{42}\ (C_2N_2)(O_2)^a, \tag{III}$$

and for Reaction 43

$$R_{-NH_3} = R_{NO} + R_{NO_2} = k_{43}\ (NH_3)(O_2)^b. \tag{IV}$$

The rates, R_{NO} and R_{NO_2}, have been determined from the flame data as have the concentration of C_2N_2, NH_3, and O_2. Generally, data were used only in the early preflame and visible flame region where both NO and NO_2 concentrations were increasing. Other NO and NO_2 formation and depletion reactions must be considered if the data downstream of the flame are included. The values of k_{42} and k_{43} derived from the data have been plotted as log k versus 1/T (Appendix B). An apparent overall activation energy was determined for each of the two reactions assuming stoichiometric quantities of O_2 for each reaction, i.e., a = 3 and b = 1.25 for Reactions 42 and 43, respectively. These data are tabulated below for several different flames.

Flame No.	Fuel	Fuel-N Additive	Apparent Act. Energy kcal/mole	Avg.
24	CO	C_2N_2	36.4	40.8
23	CO	C_2N_2	45.2	
22	CO	NH_3	54.9	57.9
21	CO	NH_3	86.6*	
12	CO	NH_3	59.1	
11	CO	NH_3	59.6	

* Omitted from averaging.

The average overall activation energy obtained for the depletion of the cyanogen in the flames is in fair to good agreement with the results obtained by other investigators. DeSoete (5) reports a value of about 40 kcal for the activation energy, while Allielet (18) reports 36 kcal for the same process. Our average E_a value of 57.9 kcal/mole for ammonia is about 26 kcal/mole higher than that obtained by DeSoete (5).

Internally, the calculated energy values, as determined from each flame, are in fair agreement for each of the species C_2N_2 and NH_3. A considerably higher activation energy is observed, however, for NH_3. This may reflect the larger energy needed to break the N-H bond of ammonia (83.7 kcal/mole) as compared to the C-C bond of cyanogen (58.6 kcal/mole). Further considerations along these lines show that in the case of cyanogen the breaking of the C-C bond would lead to CN (or NCO) formation. Studies have indicated that the subsequent reaction $CN + O_2 = NCO + O$, requires no activation energy (19). On the other hand, assuming NH radicals are derived from the NH_3, the reaction $NH + O_2 = HNO + O$, is reported to have an activation energy of approximately 13 kcal/mole (19). From these considerations, it appears that NH_3 would require more energy to produce NO than would cyanogen.

Thus, the data indicate that the fuel-N species with cyanogen-type bonding require less activation energy to produce NO thereby allowing more NO to form at lower flame temperatures than fuel-N species with N-H bonding similar to NH_3. However, one must also consider an alternate reaction in the conversion of fuel-N materials to N-containing products, that is, the general reaction

$$F\text{-}N + NO = N_2 \text{ and/or } N_2O + \text{products.}$$

It appears from our studies, that for F-N = C_2N_2, the above reaction progressively dominates as the maximum flame temperature is lowered, i.e., less NO is formed at the lower flame temperatures. This is not the case for F-N = NH_3 where most of the ammonia appears to be converted to NO even at the lower flame temperature. However, because sufficiently high temperatures and long residence times are generally encountered in the most commonly used furnaces and burner equipment, the end results will likely be the same for C_2N_2 or NH_3, i.e., at comparable fuel-N concentrations, the total NO_x in the flue gases will be about the same for C_2N_2 or NH_3.

SECTION V

SUMMARY

Water-stabilized CO flames have been probed in the presence and absence of fuel-N compounds. In the absence of additives, the CO flames produced a "prompt NO" in accordance with the Zeldovich process if one assumes a diffusion of excess O atoms into the visible flame region; NO_2 was also produced in each flame except for the O_2-rich high temperature, high velocity flame without additives. In every case, the NO_2 appeared early in the flame reactions, producing the same early NO_2 phenomena observed in hydrocarbon flames. The appearance of early NO_2 was confirmed by adding NO to the cold gases of CO flames and observing the depletion of NO and subsequent formation of NO_2 in the early flame reactions. As in hydrocarbon flames, the HO_2 radical is postulated as the species responsible for NO_2 formation in the CO flames via $NO + HO_2 = NO_2 + OH$. The HO_2 radicals are derived from the water vapor used to stabilize the CO flames. The addition of C_2N_2 or NH_3 to the CO flames produced large quantities of NO. On the other hand, little NO_2 was produced from the C_2N_2 molecules although increased residence time in the flames increased the NO_2 production. More NO_2 was produced in the presence of NH_3, but only when argon was used as a diluent. Using N_2 as a diluent appeared to suppress NO_2 formation in the flames with NH_3 but did not affect NO formation. The formation and depletion of NO and NO_2 in the CO flames can be expressed by the following equations

$$CN + O_2 \begin{cases} \rightarrow NO + CO \\ \rightarrow NCO + O \end{cases}$$

$$NCO + O \rightarrow NO + CO$$

$$NH + O_2 = NO + OH$$

$$NO + HO_2 = NO_2 + OH$$

$$NO_2 + O,H = NO + O_2,OH.$$

An alternate reaction producing essentially inert N-containing products is suggested in the pyrolysis of fuel-N compounds, especially at lower flame temperatures

$$F\text{-}N + NO = N_2,\ N_2O + \text{products}.$$

The importance of each reaction varies from flame to flame, depending on the overall flame conditions. Apparent activation energies representing overall oxidation of C_2N_2 and NH_3 to NO and NO_2 in the flames were determined as 40.8 kcal/mole and 57.9 kcal/mole, respectively.

Nitrogen oxide formation and depletion processes in the CO flames are very similar to those in hydrocarbon flames. The major difference appears to be in the amount of transient NO_2 formed in the flames. Generally, the CO flames produce less NO_2 than do similar hydrocarbon flames. This can be related to less HO_2 production in the hydrogen-deficient CO flames. Ultimately, however, the end results are similar to both CO and hydrocarbon flames; at low ppm fuel-N levels, most of the fuel-N appears as NO in the postflame gases. Small amounts of NO_2 are sometimes present in the postflame gases of the O_2-rich flames.

The flame data show high NO_2 emission levels can result from the CO flames if rapid quenching occurs near the flame front. This latter situation often occurs in open air flames of various geometries. Rapid quenching must be avoided if NO_2 levels are to be kept low in the emission gases.

There are many unanswered questions insofar as a full understanding of NO_x chemistry in CO flames is concerned. These studies of the NO_x flame chemistry, however, have provided new information in this area as summarized above. Certainly, the requirement of H-containing compounds to stabilize the CO flames appears to produce conditions in these flames similar to those observed in hydrocarbon flames insofar as the nitrogen oxide chemistry is concerned. In order to get more information on the

role of the HO_2 radical in nonhydrocarbon flames, a dry CO-C_2N_2 flame or even a pure C_2N_2 or COS flame may be required.

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APPENDIX A

FLAME PROFILES

APPENDIX A

FLAME PROFILES

a = Flame holder

b = Bottom edge of flame

c = Top edge of flame

Flames with similar CO, CO_2, O_2, and temperature profiles

Flame Nos: 1, 3, 5*, 7

2, 4, 6*, 8

9*, 11, 13

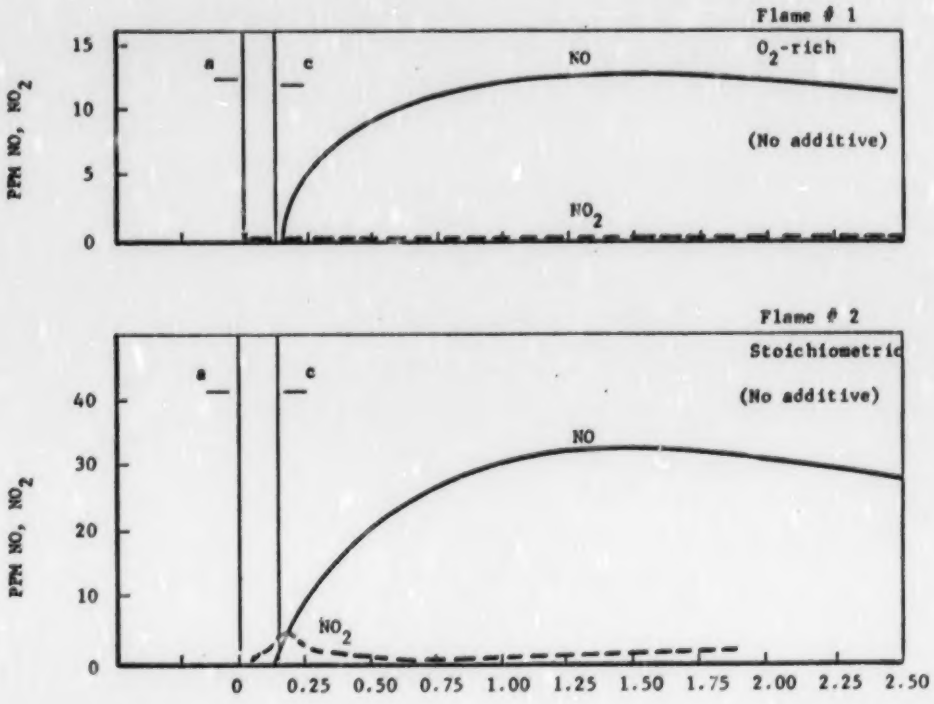
10*, 12, 14

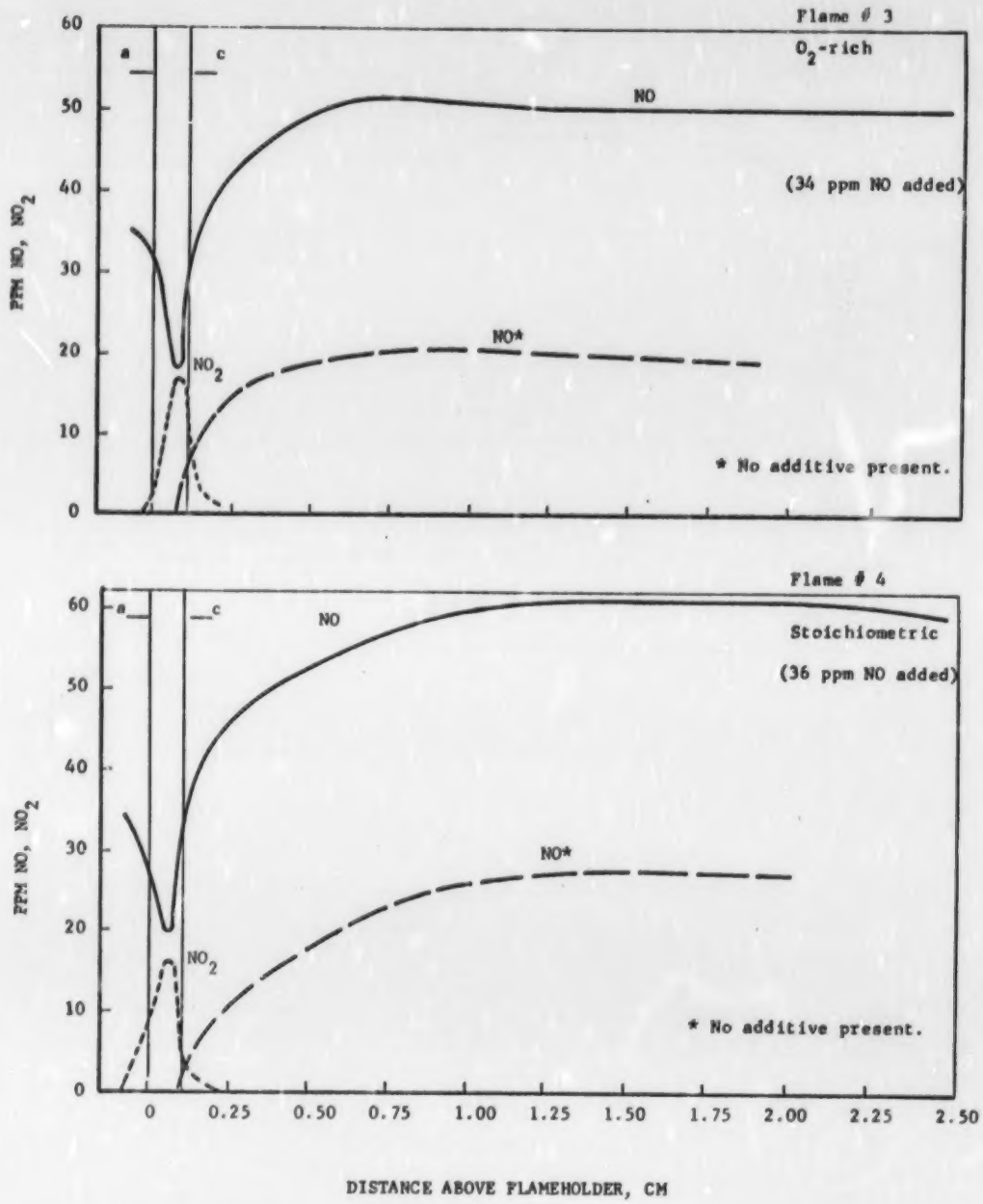
19*, 21, 23

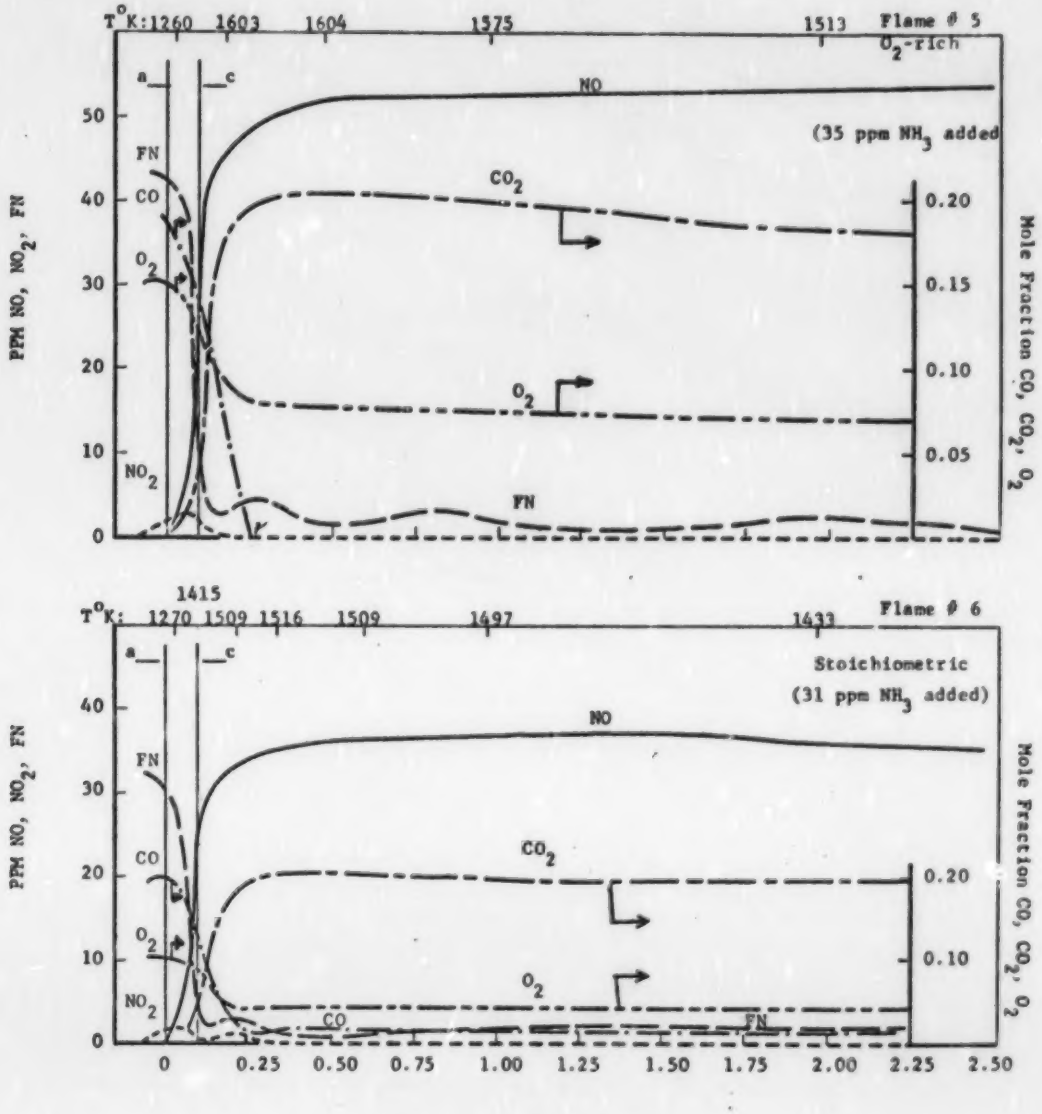
20*, 22, 24

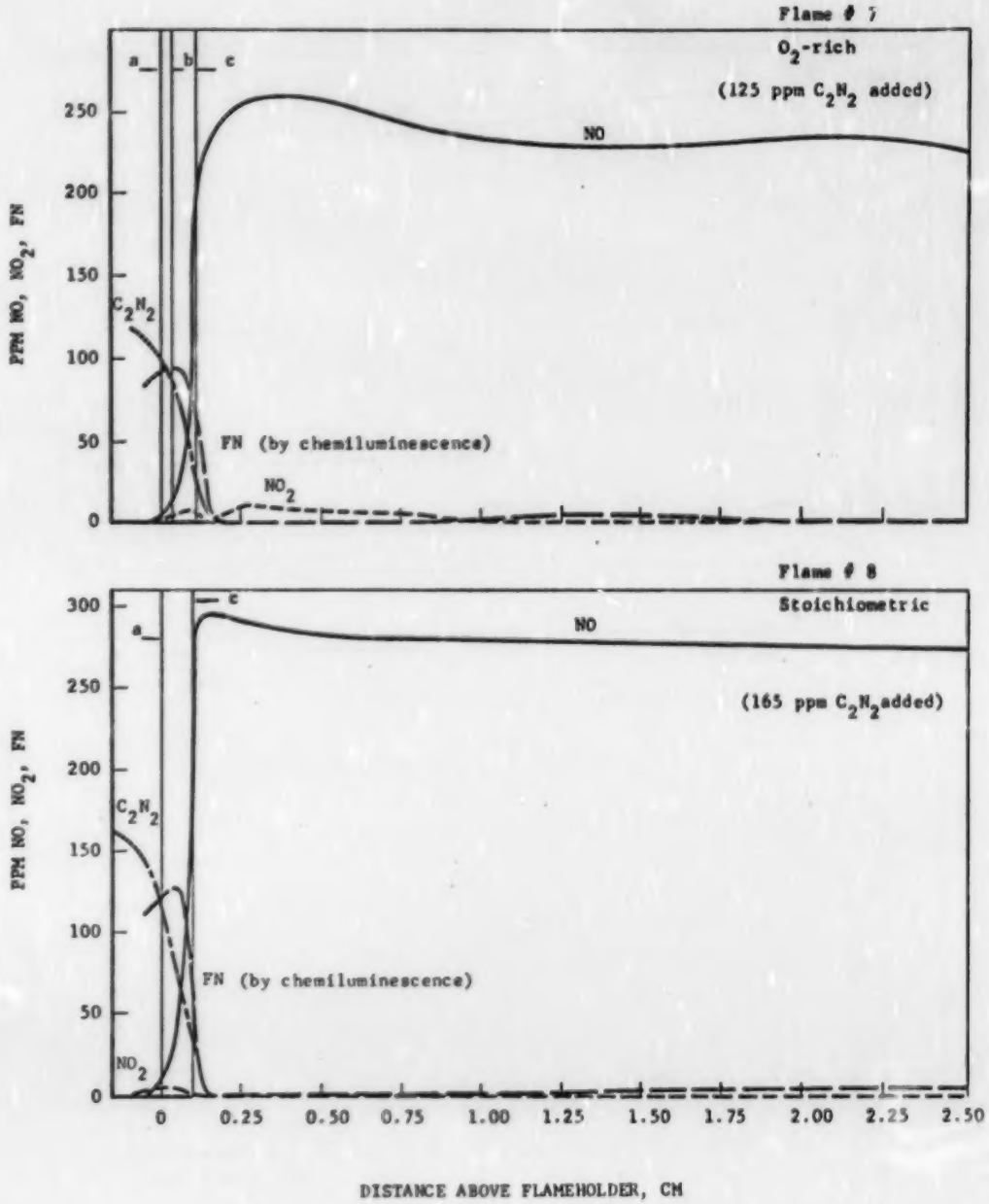
---

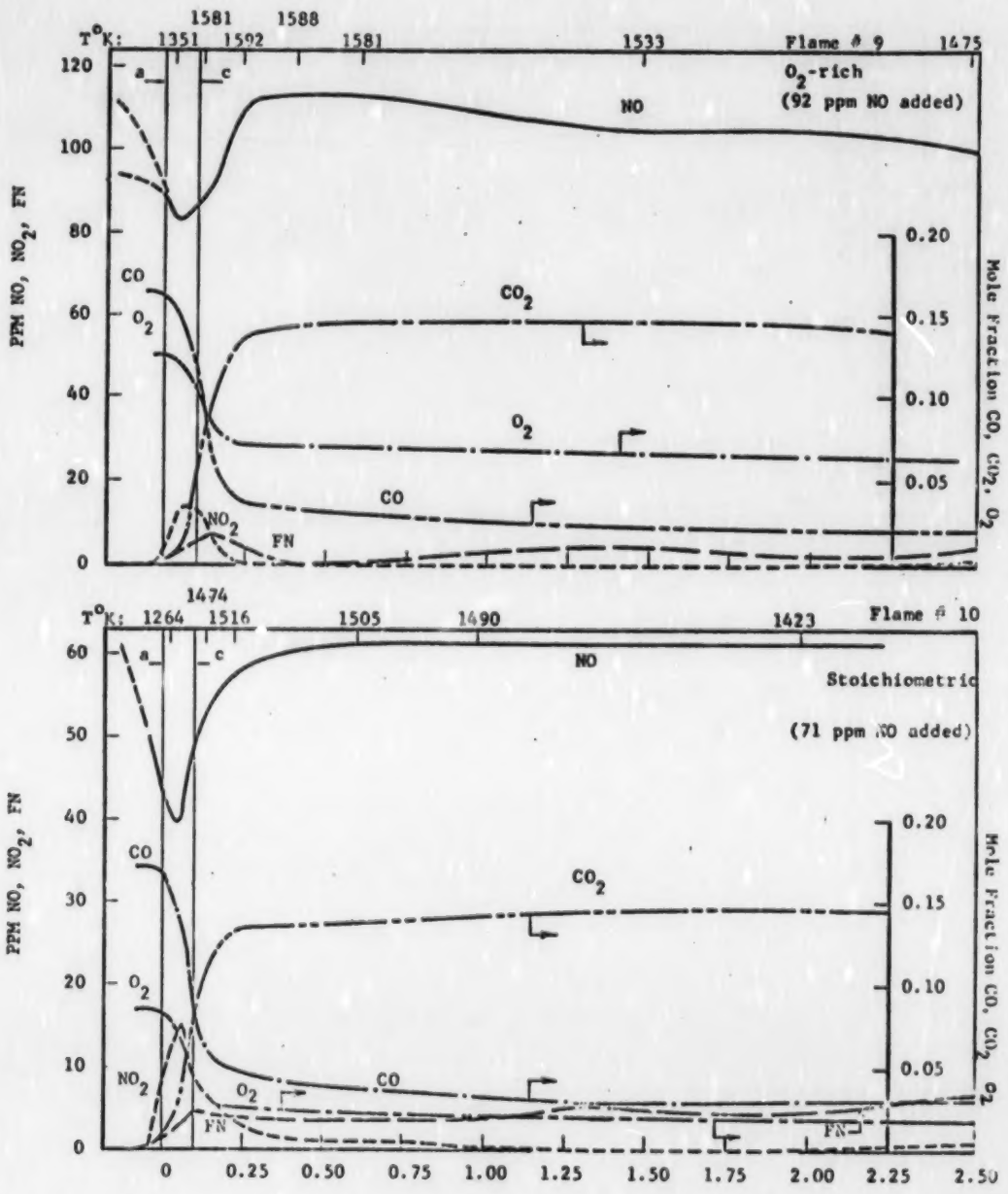
* Detailed profiles presented.

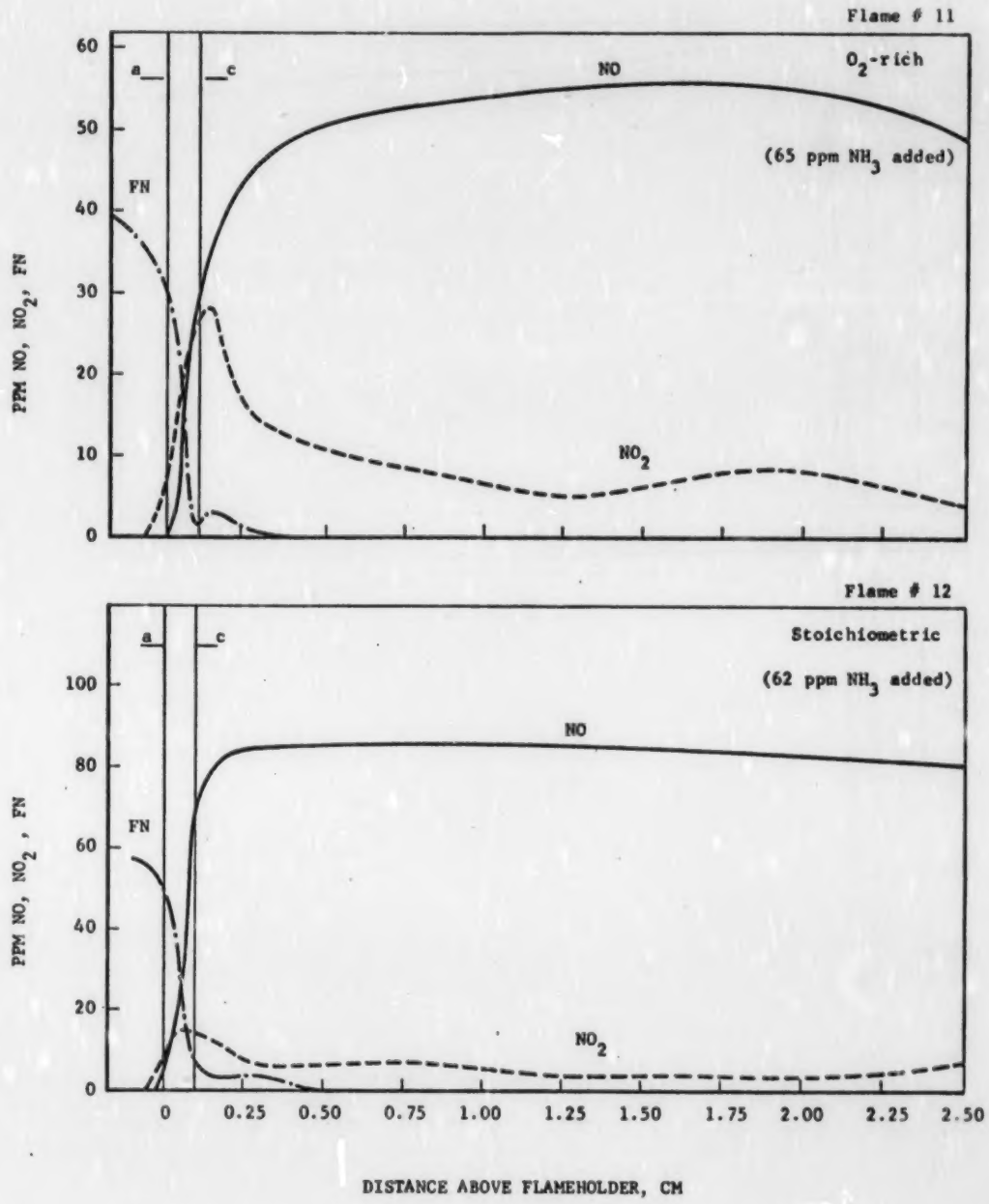

Flame # 1
O_2-rich
(No additive)
NO
NO_2
a
c
15
10
5
0
PPM NO, NO_2
Flame # 2
Stoichiometric
(No additive)
NO
NO_2
a
c
40
30
20
10
0
PPM NO, NO_2
0
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
2.25
2.50
DISTANCE ABOVE FLAMEHOLDER, CM

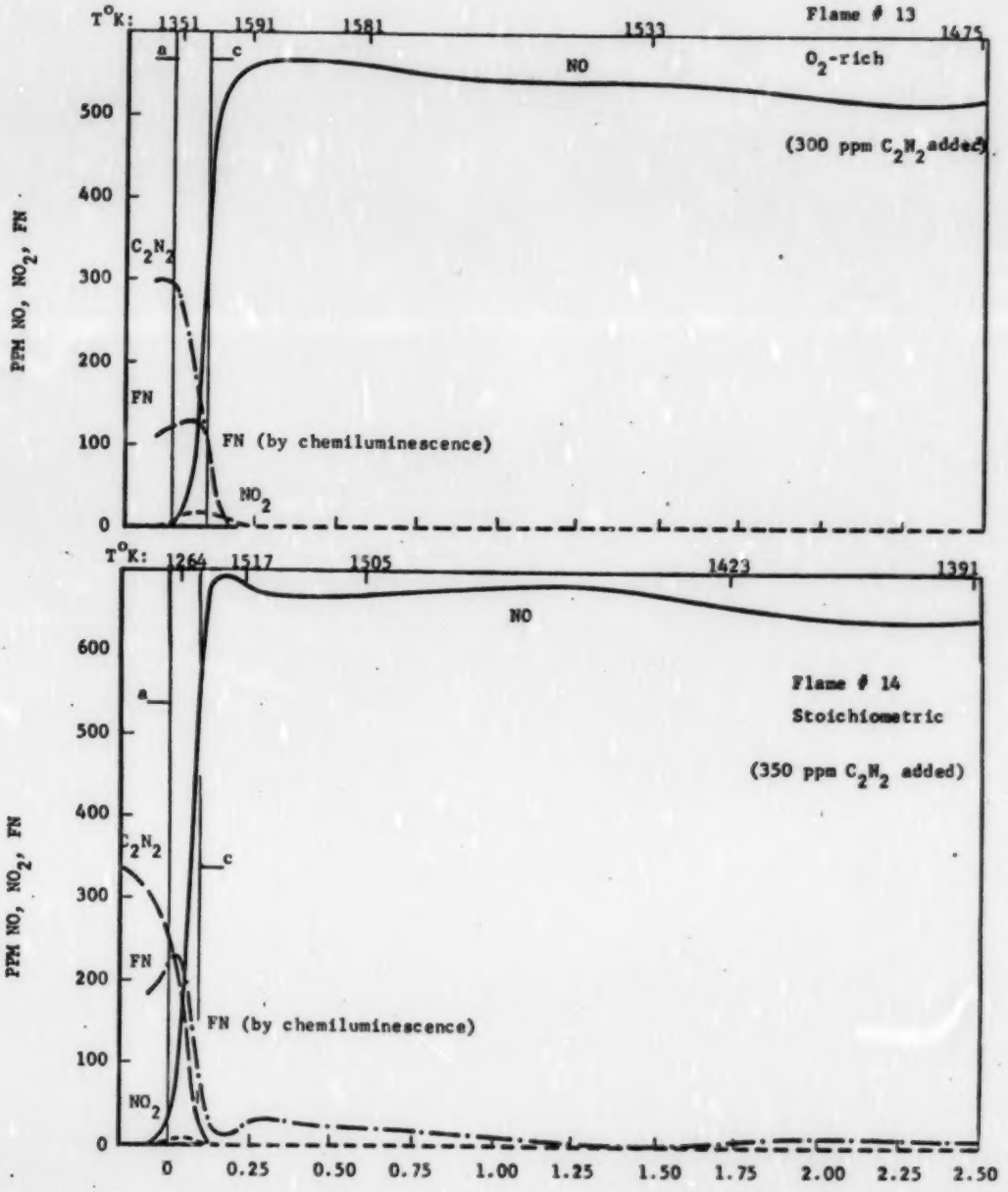

Flame # 3
O_2-rich
a
c
NO
(34 ppm NO added)
NO*
NO_2
* No additive present.
PPM NO, NO_2
60
50
40
30
20
10
0
Flame # 4
Stoichiometric
(36 ppm NO added)
0
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
2.25
2.50
DISTANCE ABOVE FLAMEHOLDER, CM

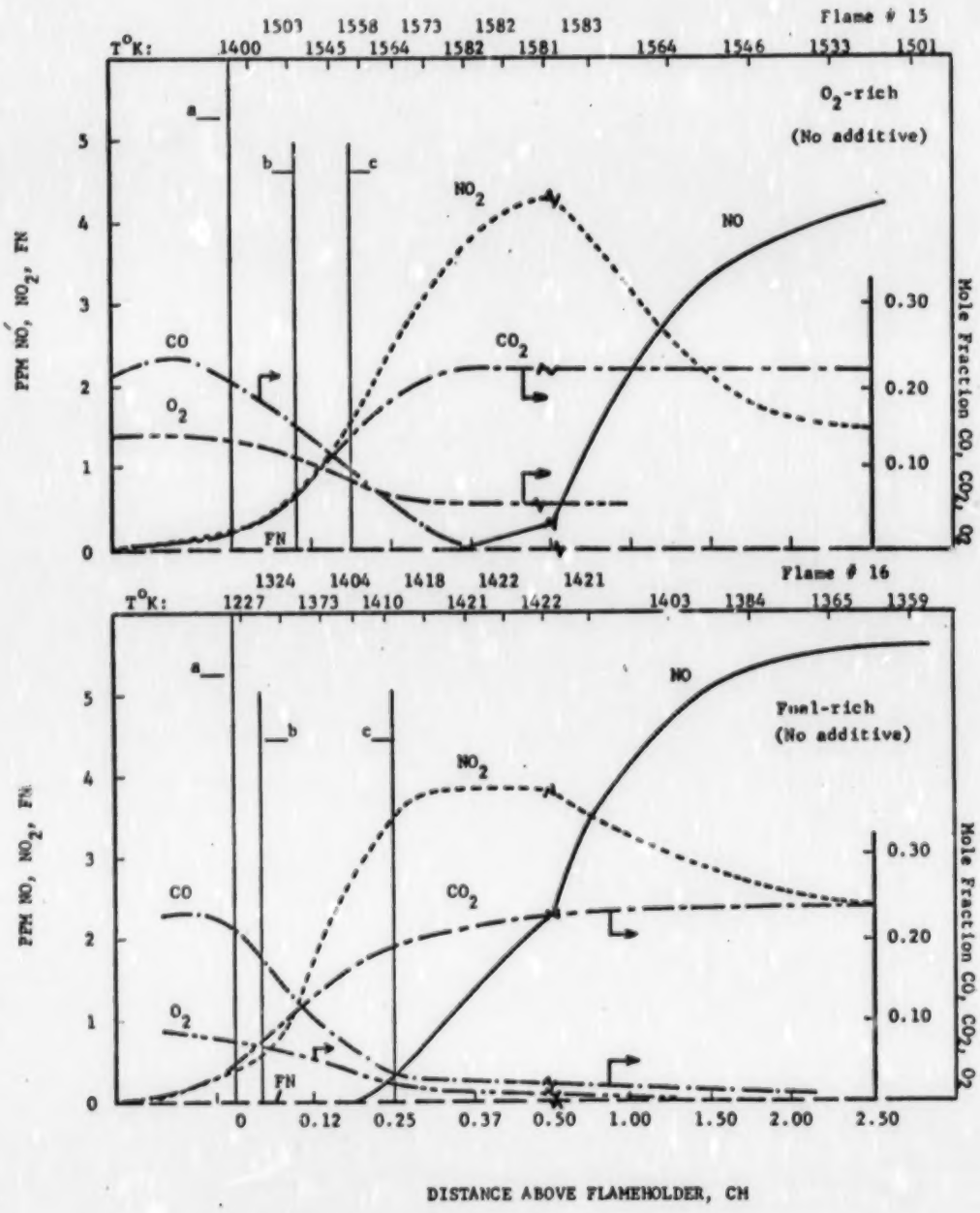

T°K: 1260 1603 1604 1575 1513
Flame # 5
O2-rich
(35 ppm NH3 added
NO
CO2
O2
FN
NO2
CO
PPM NO, NO2, FN
Mole Fraction CO, CO2, O2
T°K: 1270 1509 1516 1509 1497 1433
1415
Flame # 6
Stoichiometric
(31 ppm NH3 added)
0 0.25 0.50 0.75 1.00 1.25 1.50 1.75 2.00 2.25 2.50
DISTANCE ABOVE FLAMEHOLDER, CM

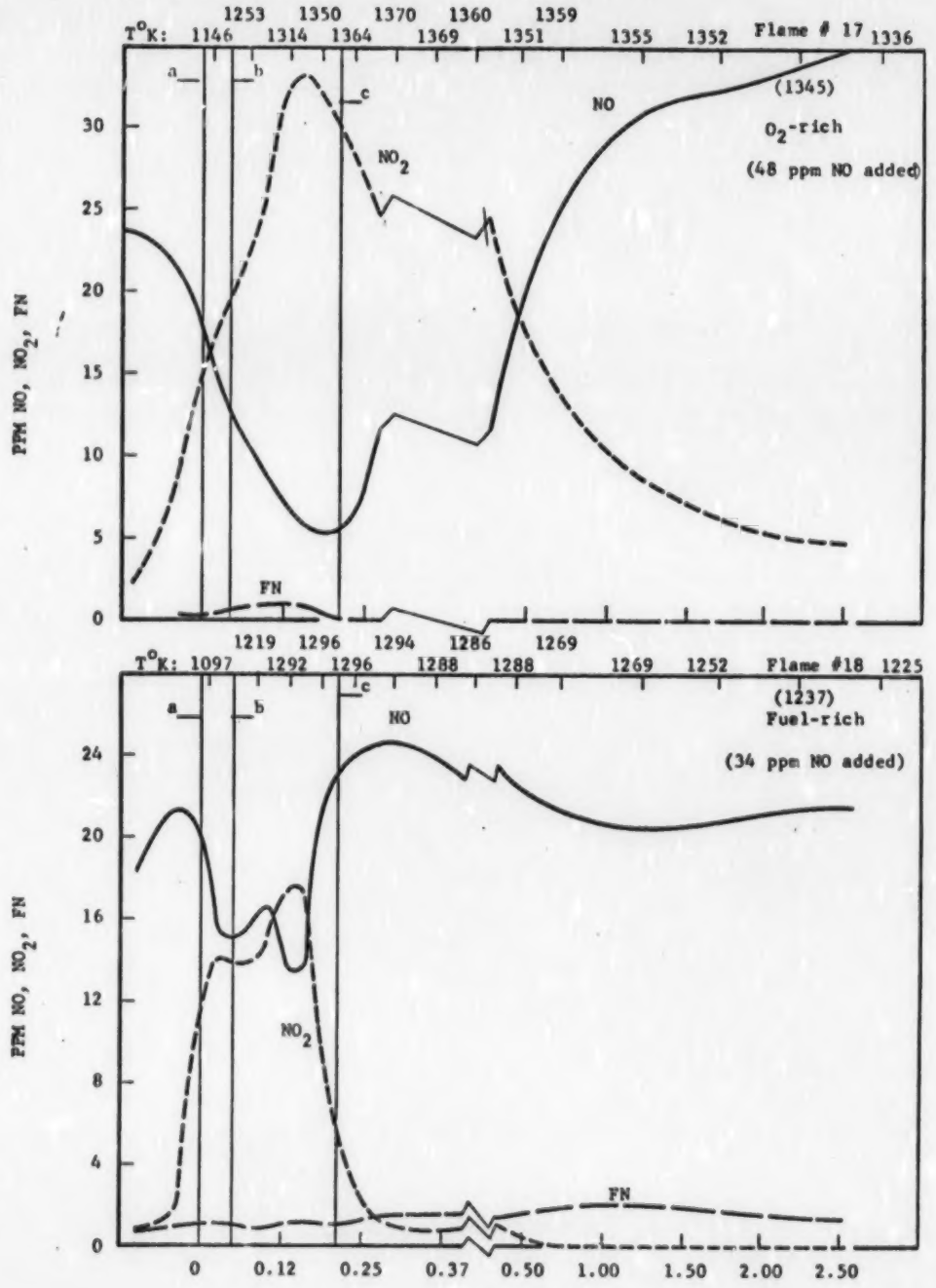

Flame # 7
O_2-rich
(125 ppm C_2N_2 added)
a
b
c
NO
C_2N_2
FN (by chemiluminescence)
NO_2
PPM NO, NO_2, FN
Flame # 8
Stoichiometric
(165 ppm C_2N_2 added)
0
50
100
150
200
250
300
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
2.25
2.50
DISTANCE ABOVE FLAMEHOLDER, CM

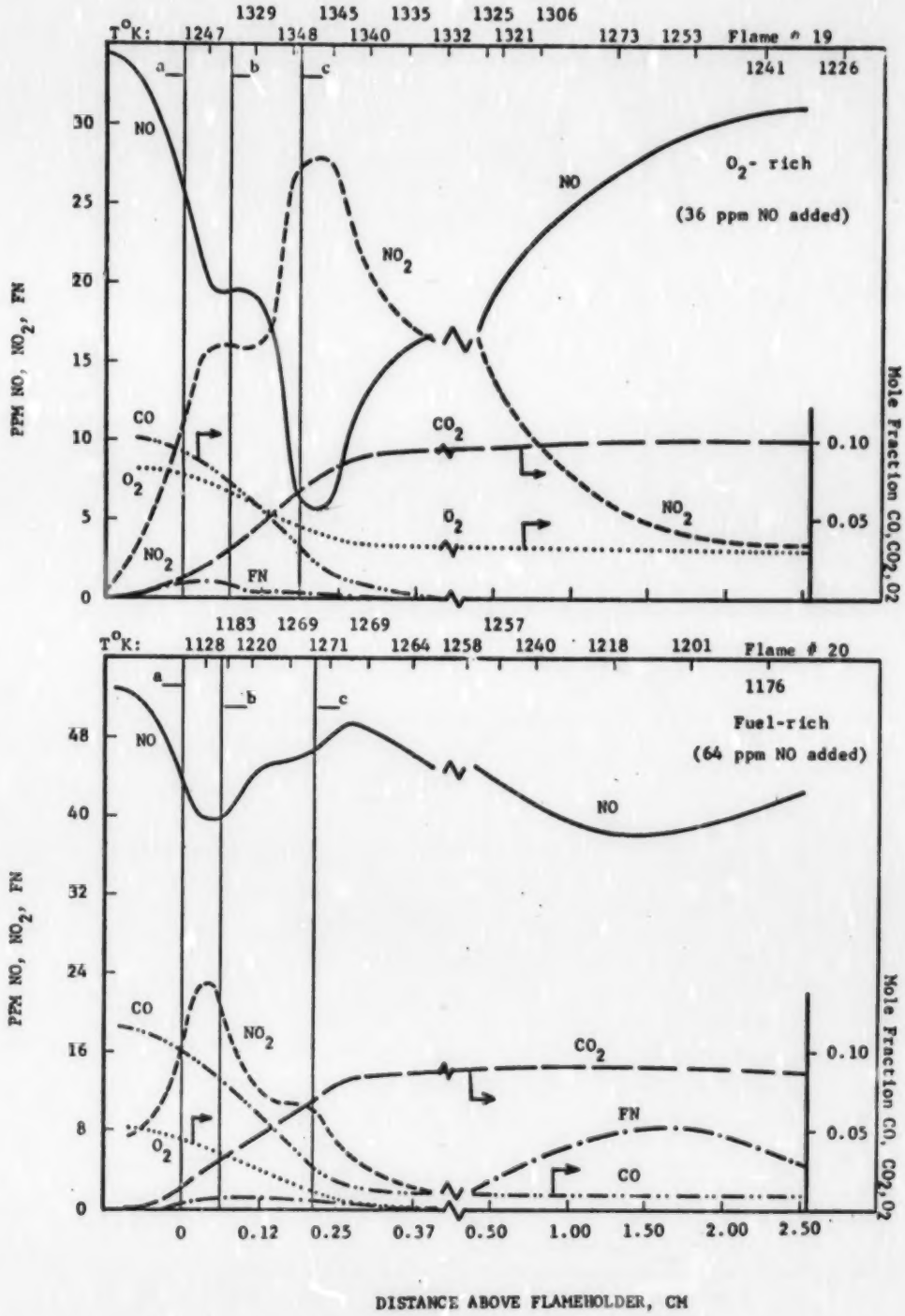

T°K: 1351 1581 1588 1592 1581 1533 Flame # 9 1475
O2-rich
(92 ppm NO added)
NO
CO2
O2
CO
NO2
FN
a
c
PPM NO, NO2, FN
Mole Fraction CO, CO2, O2
T°K: 1264 1474 1516 1505 1490 1423 Flame # 10
Stoichiometric
(71 ppm NO added)
0 0.25 0.50 0.75 1.00 1.25 1.50 1.75 2.00 2.25 2.50
DISTANCE ABOVE FLAMEHOLDER, CM

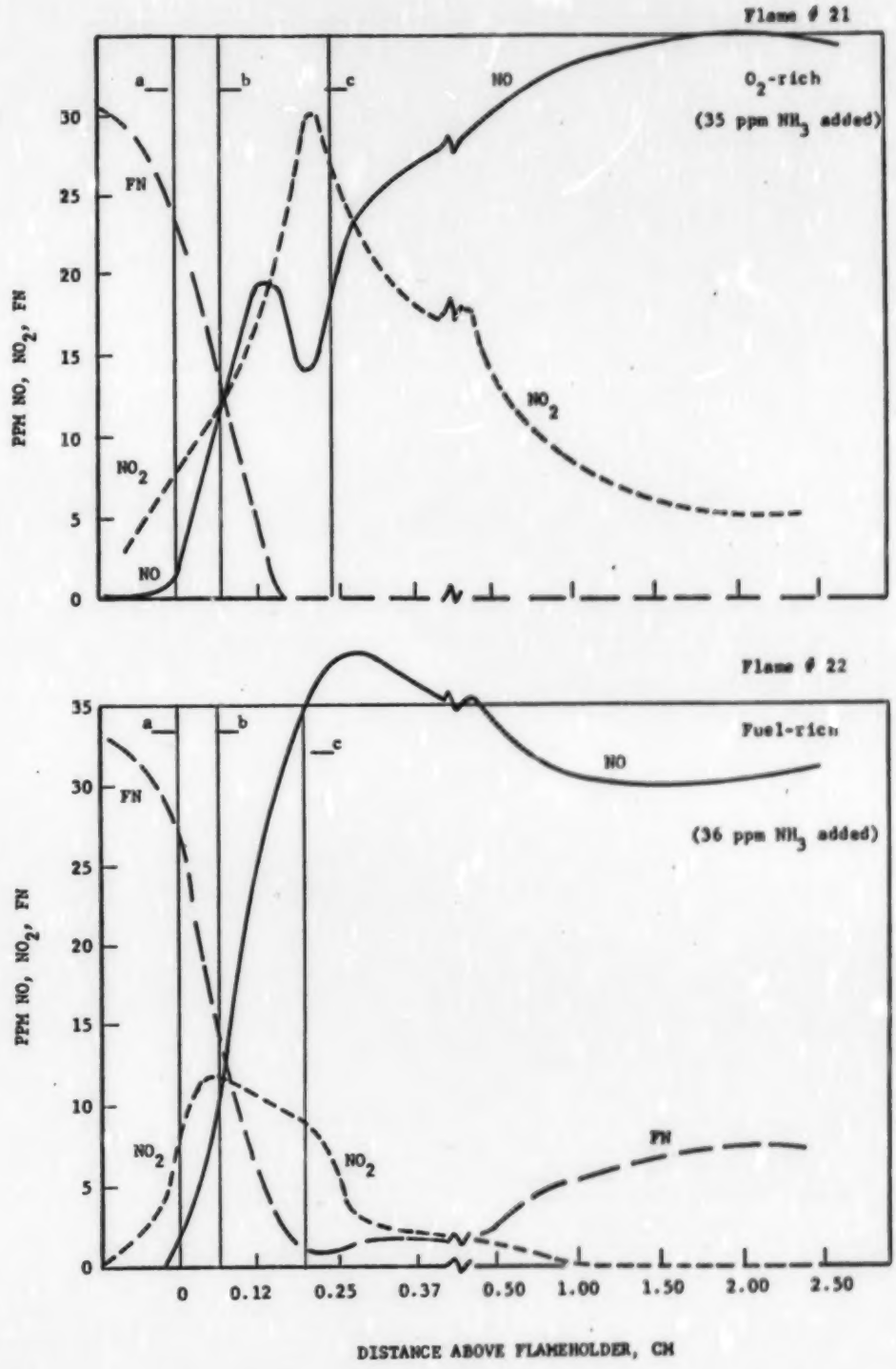

Flame # 11
O_2-rich
(65 ppm NH_3 added)
a
c
NO
FN
NO_2
PPM NO, NO_2, FN
Flame # 12
Stoichiometric
(62 ppm NH_3 added)
a
c
NO
FN
NO_2
PPM NO, NO_2, FN
0
10
20
30
40
50
60
0
20
40
60
80
100
0
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
2.25
2.50
DISTANCE ABOVE FLAMEHOLDER, CM

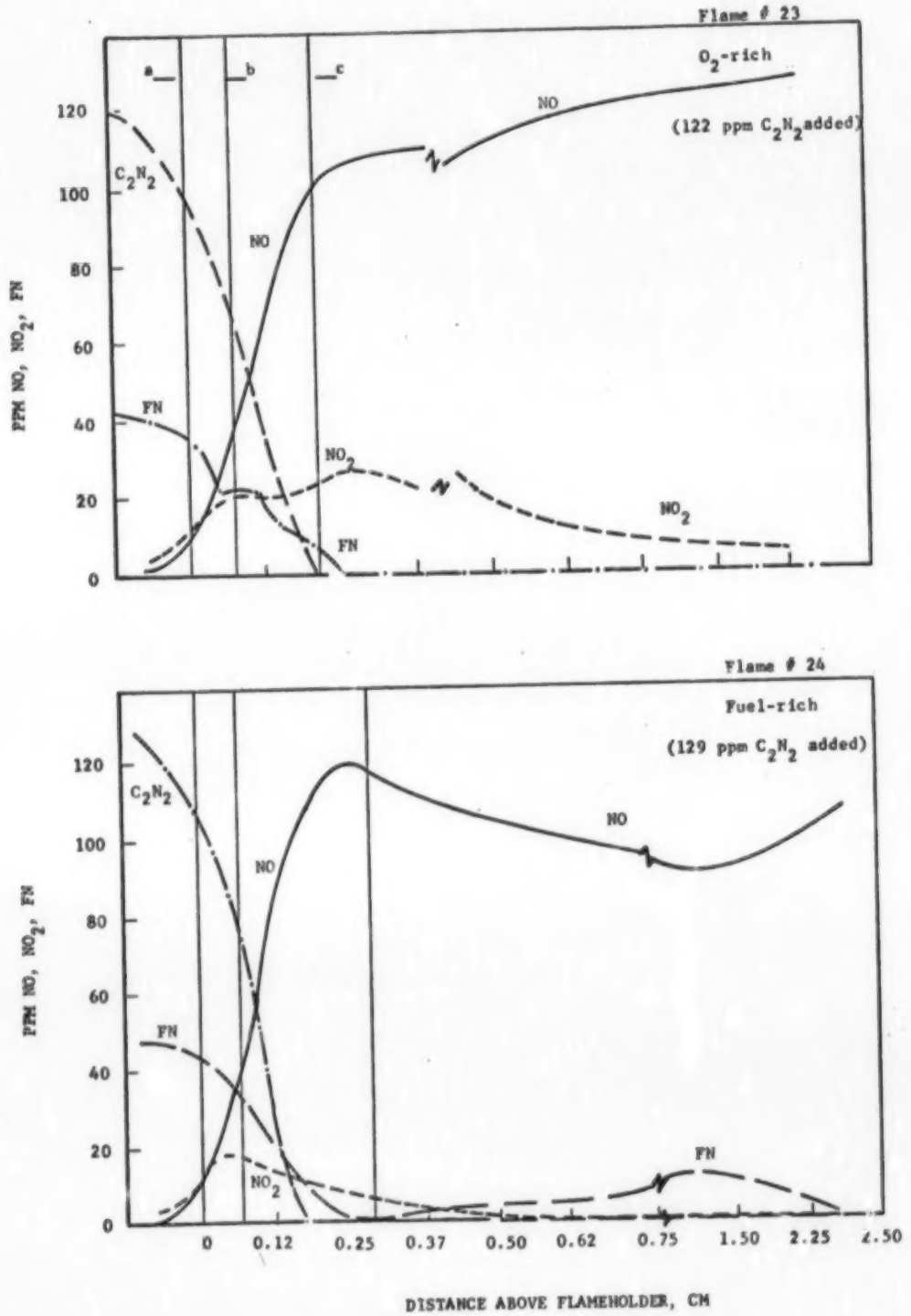

T°K: 1351 1591 1581 1533 1475
Flame # 13
O2-rich
NO
(300 ppm C2N2 added)
a
c
C2N2
FN
FN (by chemiluminescence)
NO2
PPM NO, NO2, FN
T°K: 1264 1517 1505 1423 1391
NO
Flame # 14
Stoichiometric
(350 ppm C2N2 added)
a
c
C2N2
FN
FN (by chemiluminescence)
NO2
PPM NO, NO2, FN
0 0.25 0.50 0.75 1.00 1.25 1.50 1.75 2.00 2.25 2.50
DISTANCE ABOVE FLAMEHOLDER, CM


Flame # 15
T°K: 1503 1558 1573 1582 1583
1400 1545 1564 1582 1581 1564 1546 1533 1501
O2-rich
(No additive)
a
b
c
NO2
NO
CO
CO2
O2
FN
PPM NO, NO2, FN
Mole Fraction CO, CO2, O2
0.30
0.20
0.10
Flame # 16
T°K: 1324 1404 1418 1422 1421
1227 1373 1410 1421 1422 1403 1384 1365 1359
Fuel-rich
(No additive)
0 0.12 0.25 0.37 0.50 1.00 1.50 2.00 2.50
DISTANCE ABOVE FLAMEHOLDER, CM


T°K: 1253 1350 1370 1360 1359
1146 1314 1364 1369 1351 1355 1352 Flame # 17 1336
a
b
c
NO
(1345)
O_2-rich
(48 ppm NO added)
NO_2
FN
PPM NO, NO_2, FN
30
25
20
15
10
5
0
T°K: 1219 1296 1294 1286 1269
1097 1292 1296 1288 1288 1269 1252 Flame #18 1225
(1237)
Fuel-rich
(34 ppm NO added)
24
20
16
12
8
4
0
0 0.12 0.25 0.37 0.50 1.00 1.50 2.00 2.50
DISTANCE ABOVE FLAMEHOLDER, CM

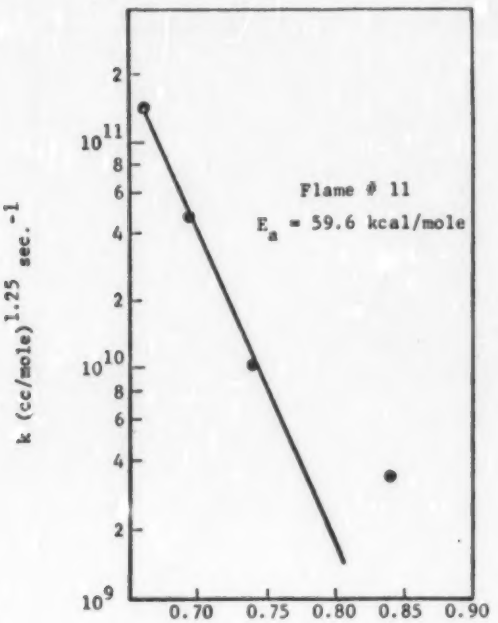

T°K: 1247 1329 1345 1348 1340 1335 1332 1325 1321 1306 1273 1253 1241 1226 Flame # 19
a
b
c
NO
NO
NO2
O2- rich
(36 ppm NO added)
NO2
CO
CO2
O2
O2
NO2
FN
0.10
0.05
PPM NO, NO2, FN
Mole Fraction CO, CO2, O2
T°K: 1128 1183 1220 1269 1271 1269 1264 1258 1257 1240 1218 1201 1176 Flame # 20
Fuel-rich
(64 ppm NO added)
NO
NO
CO
NO2
CO2
FN
O2
CO
0.10
0.05
0 0.12 0.25 0.37 0.50 1.00 1.50 2.00 2.50
DISTANCE ABOVE FLAMEHOLDER, CM

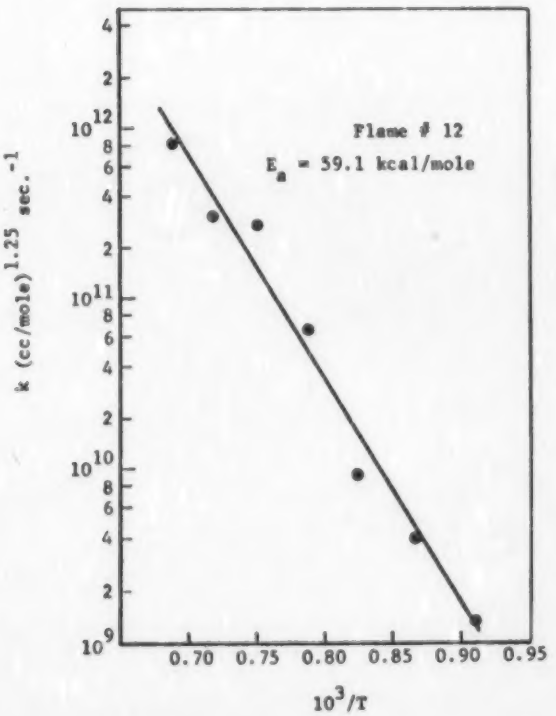

Flame # 21
a
b
c
NO
O_2-rich
(35 ppm NH_3 added)
FN
NO_2
NO
NO_2
PPM NO, NO_2, FN
0
5
10
15
20
25
30
Flame # 22
Fuel-rich
NO
(36 ppm NH_3 added)
FN
NO_2
NO_2
FN
PPM NO, NO_2, FN
0
5
10
15
20
25
30
35
0
0.12
0.25
0.37
0.50
1.00
1.50
2.00
2.50
DISTANCE ABOVE FLAMEHOLDER, CM

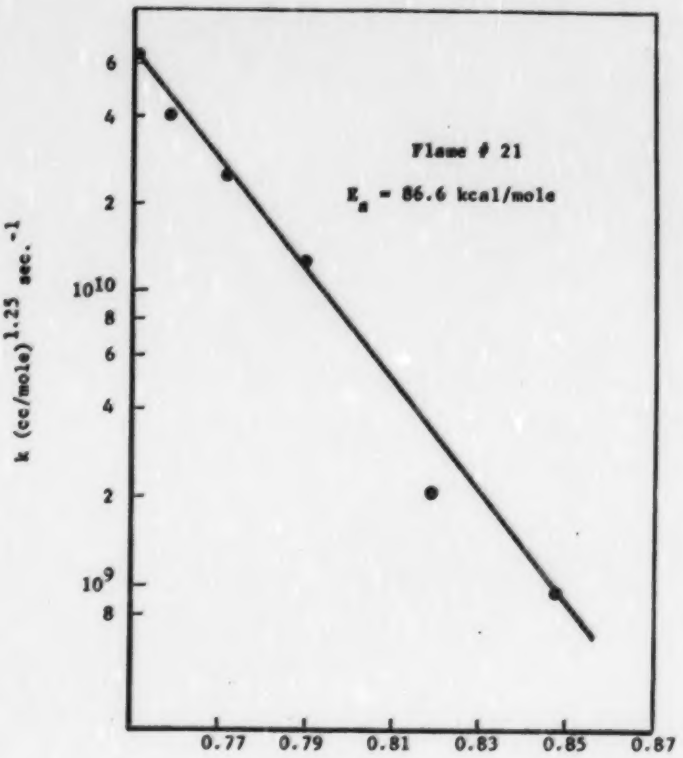

Flame # 23
O_2-rich
(122 ppm C_2N_2 added)
a
b
c
C_2N_2
NO
FN
NO_2
PPM NO, NO_2, FN
0
20
40
60
80
100
120
Flame # 24
Fuel-rich
(129 ppm C_2N_2 added)
0
0.12
0.25
0.37
0.50
0.62
0.75
1.50
2.25
2.50
DISTANCE ABOVE FLAMEHOLDER, CM

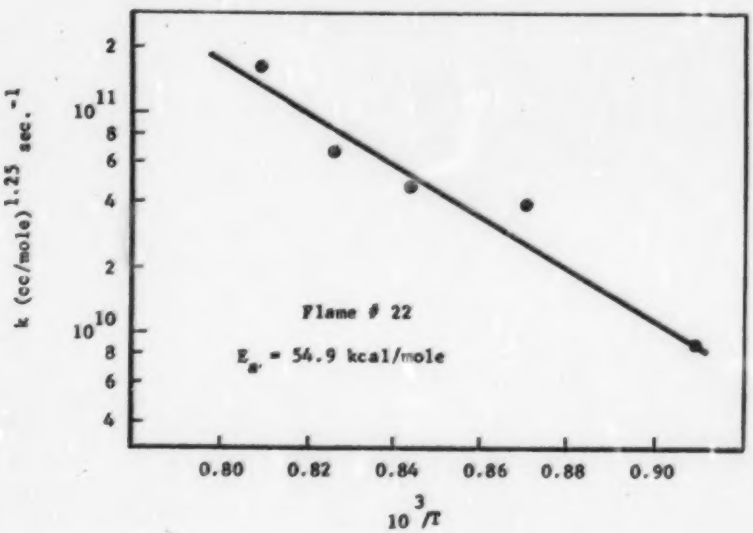
APPENDIX B

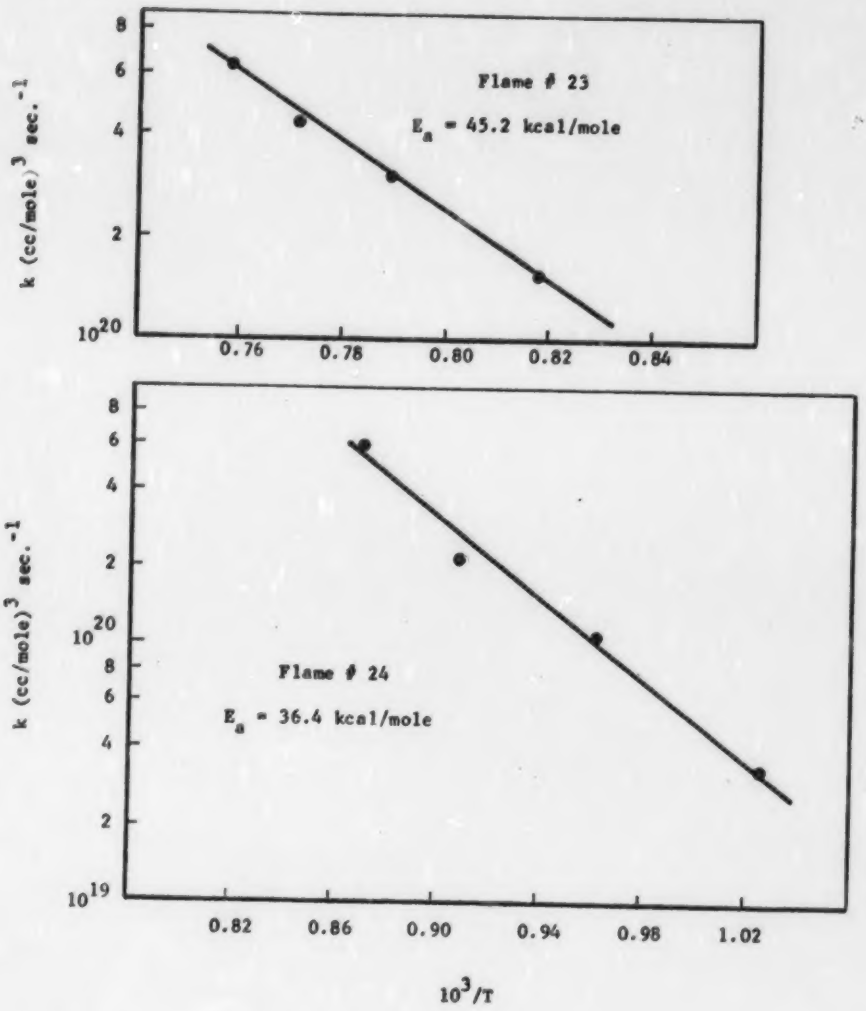
ARRHENIUS PLOTS


Flame # 11
E_a = 59.6 kcal/mole
k (cc/mole)$^{1.25}$ sec.$^{-1}$
10^{11}
10^{10}
10^{9}
0.70
0.75
0.80
0.85
0.90


Flame # 12
E_a = 59.1 kcal/mole
k (cc/mole)$^{1.25}$ sec.$^{-1}$
10^{12}
10^{11}
10^{10}
10^{9}
0.70
0.75
0.80
0.85
0.90
0.95
$10^3/T$


Flame # 21
E_a = 86.6 kcal/mole
k (cc/mole)$^{1.25}$ sec.$^{-1}$
6
4
2
10^{10}
8
6
4
2
10^{9}
8
0.77
0.79
0.81
0.83
0.85
0.87


Flame # 22
E_a = 54.9 kcal/mole
k (cc/mole)$^{1.25}$ sec.$^{-1}$
2
10^{11}
8
6
4
2
10^{10}
8
6
4
0.80
0.82
0.84
0.86
0.88
0.90
$10^{3}/T$


Flame # 23
E_a = 45.2 kcal/mole
k (cc/mole)^3 sec.$^{-1}$
8
6
4
2
10^{20}
0.76
0.78
0.80
0.82
0.84
Flame # 24
E_a = 36.4 kcal/mole
k (cc/mole)^3 sec.$^{-1}$
8
6
4
2
10^{20}
8
6
4
2
10^{19}
0.82
0.86
0.90
0.94
0.98
1.02
$10^3/T$